Kondo Behavior of U in CaB_6

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(Dated: February 2, 2008)

Abstract

Replacing U for Ca in semiconducting CaB_6 at the few at.% level induces metallic behaviour and Kondo-type phenomena at low temperatures, a rather unusual feature for U impurities in metallic hosts. For $Ca_{0.992}U_{0.008}B_6$, the resistance minimum occurs at $T = 17$ K. The subsequent characteristic logarithmic increase of the resistivity with decreasing temperature merges into the expected T^2 dependence below 0.8 K. Data of the low-temperature specific heat and the magnetization are analyzed by employing a simple resonance-level model. Analogous measurements on LaB_6 with a small amount of U revealed no traces of Kondo behavior, above 0.4 K.

The Kondo phenomenon, a many-body effect affecting the conduction electrons via their interaction with localized magnetic moments, is notorious for d-transition metal impurities in simple metals [1]. Kondo behaviour is also often observed in metallic compounds, in which a small number of cation sites is occupied by rare-earth ions, usually trivalent Ce. A well known case for this type of dilute Kondo systems is (La,Ce)B_6, with a Ce-content on the few percent level. At low temperatures, all the typical Kondo anomalies, as for example in the resistivity [2] or in the specific heat [3], were observed. By adding the light actinide element U instead of the lanthanide Ce into the same metallic matrix does not lead to any Kondo anomalies, however [4]. This reflects the notorious observation that magnetic moments due to 5f electrons do not induce a Kondo effect in a metallic host with a large number of itinerant charge carriers. It is assumed that this is caused by a broadening of the 5f-states via hybridization with the conduction band states, and hence the f-electrons loose their localized character. In this work we demonstrate that the situation changes if U occupies a few cation sites in the low-carrier density matrix CaB_6, with a background density of conduction electrons of the order of 10^{-4} per unit cell [5]. Our data on the low-temperature behaviour of the electrical resistivity, the magnetic susceptibility and magnetization as well as the specific heat clearly indicate that 5f electron moments may, under special circumstances, induce the classical Kondo effect.

A single-crystalline sample of $Ca_{0.992}U_{0.008}B_6$ was grown in a flux of Al, using the necessary high-purity starting elements U, Ca and B. For measurements of the resistivity between 0.4 and 300 K, the sample was contacted at four small spots by a silver-epoxy glue and a low-frequency ac-method was applied. The specific heat was measured between 0.4 and 12 K, using a relaxation-type method. Measurements of the susceptibility and the magnetization, up to 5.5 T, were performed using a commercial SQUID magnetometer. In order to avoid the influence of possible magnetic impurities at the surface, the sample was etched several times for a short duration in diluted nitric acid.

The main frame of Fig. 1 shows the temperature dependence of the resistivity $\rho(T)$ for $Ca_{0.992}U_{0.008}B_6$ in zero applied magnetic field and for temperatures between 0.4 and 300 K. Below room temperature, ρ decreases almost linearly with decreasing T, reaches a minimum at $T = T_{min} \approx 17$ K and subsequently increases again with decreasing temperature, tending to a finite value at $T = 0$ K.

At $T > 30$ K, $\rho(T)$ is best described by employing a model that was recently introduced for

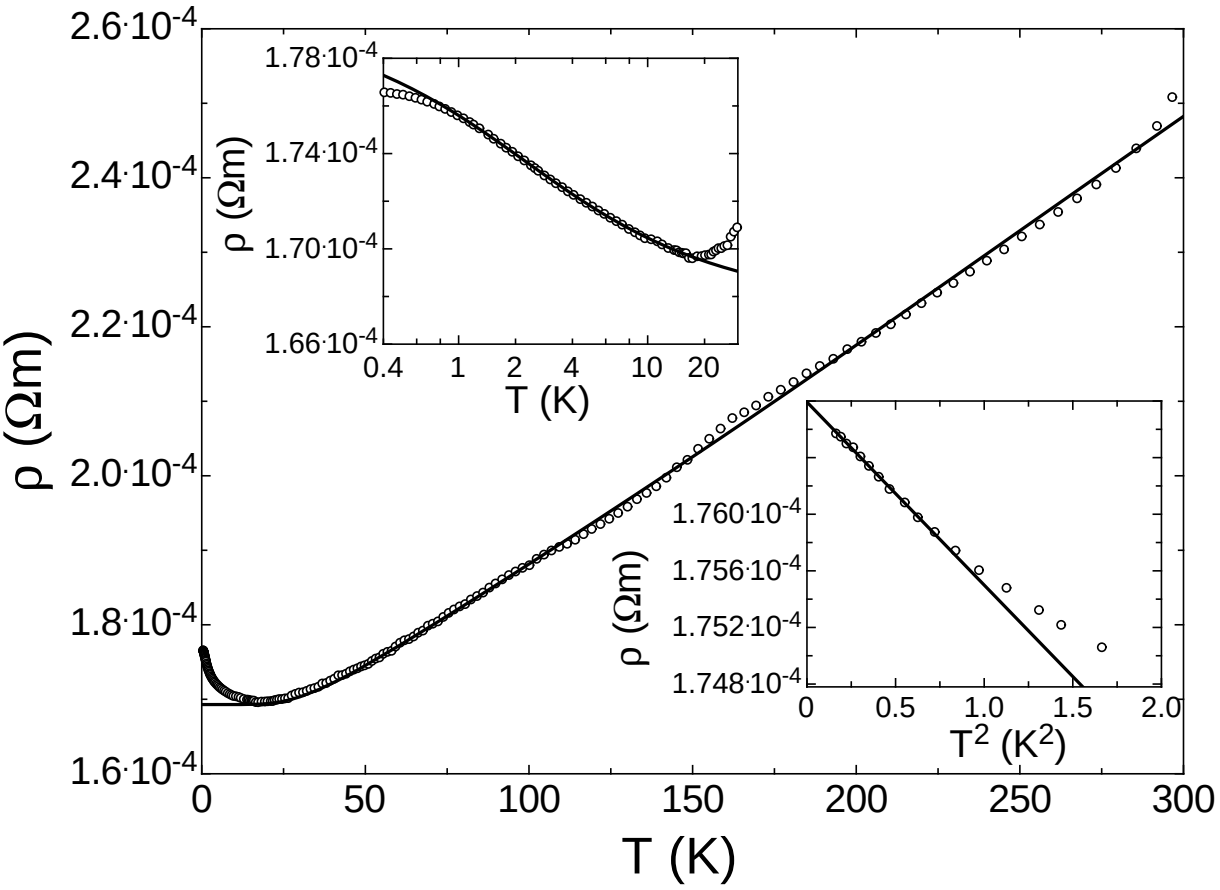

FIG. 1: Temperature dependence of the electrical resistivity for $Ca_{0.992}U_{0.008}B_6$ in zero magnetic field. The solid line in the main frame represents the result of the calculation explained in the text. The left upper inset shows $\rho(T)$ for $T < 30$ K and the fit employing eq. 1. The right lower inset emphasizes the T^2 dependence of ρ for $T < 0.8$ K.

handling Eu-based hexaborides [6, 7]. The conduction electrons are assumed to be scattered by disordered magnetic moments, lattice vibrations and lattice defects. Considering the low concentration of magnetic U ions and temperatures exceeding 30 K, our analysis establishes a constant spin-disorder resistivity and a defect resistivity $\rho_d = 1.68{\cdot}10^{-4}$ Ωm. The phonon spectrum of the B_6-lattice is assumed to be that of a Debye solid with a Debye temperature $\Theta_D = 1160$ K [8]. The motion of the Ca and U ions is taken into account by two independent harmonic oscillators with Einstein-temperatures of $\Theta_E^{Ca} = 373$ K [7] and $\Theta_E^U = 137$ K, respectively. The solid line in Fig. 1 represents the fit to $\rho(T)$ according to this calculation.

Below $T \approx 17$ K, the resistivity increases again with decreasing T. Between 2.5 K and 10 K, this increase is very close to logarithmic. In non-magnetic host materials with magnetic

impurities, such a T-dependence is usually attributed to the formation of virtual bound states of the conduction electrons at the magnetic sites. According to Hamann [9], the magnetic impurity scattering leads to a resistivity

$$\rho_{imp} = \frac{\rho_0}{2}\left\{1 - \frac{ln(T/T_K)}{[(ln(T/T_K))^2 + \pi^2 S(S+1)]^{1/2}}\right\} \ , \tag{1}$$

where T_K is the Kondo temperature and S is the spin of the magnetic impurity. The upper inset in Fig. 1 shows $\rho(T)$ for $T < 30$ K. The fit according to eq. 1, displayed as the solid line in the inset, yields $T_K = 2.0 \pm 0.1$ K and $S = 1/2$, indicating a doublet ground state of the crystal-field split U 5f electron multiplet.

In compounds, U adopts a tri- or tetravalent configuration. Under the simplifying assumption that Hund's rule and Russel-Saunders coupling are valid, free U^{4+}-ions carry a total angular momentum of $J = 4$. Lea, Leask and Wolf [10] established the ground states for various values of J in a variety of different cubic crystal field environments. For $J = 4$ the ground state is either a singlet or a triplet. Free U^{3+}-ions adopt an angular momentum $J = 9/2$. For a value of the crystal field parameter $x < 0.4$, the CEF split ground state is the doublet state Γ_6. A spin value of $S = 1/2$ obtained from fitting eq. 1 to our data suggests that U most likely adopts the trivalent $5f^3$ configuration and the ground state is the Γ_6-doublet.

It is expected that at $T \ll T_K$, the Kondo system exhibits a crossover to Fermi liquid behavior [11]. For the n-channel Kondo model with $n = 2S$, the relevant contribution to ρ is [12]

$$\rho_{imp}(T) = \rho_{imp}(0)\left\{1 - \left(\frac{\pi^2}{12T_L}\right)^2 (4n+5)T^2\right\} \ . \tag{2}$$

In our case, $n = 1$ and the corresponding fit, shown in the lower inset of Fig. 1, results in $T_L \sim T_K \cdot \pi \approx 6.0$ K. This corresponds to $T_K \approx 1.9$ K, in very good agreement with the value mentioned above. Since ρ_{imp} strongly depends on the magnitude of the residual resistivity, this analysis is less reliable, however.

Further evidence for the Kondo behavior of U in CaB_6 is obtained from measurements of the specific heat at low temperatures. Fig. 2 shows, on double-logarithmic scales, the measured specific heat $C_p(T)$ in zero magnetic field for the same specimen of $Ca_{0.992}U_{0.008}B_6$ between 0.4 and 12 K. The broad bell-shaped anomaly, observed at low T with a maximum

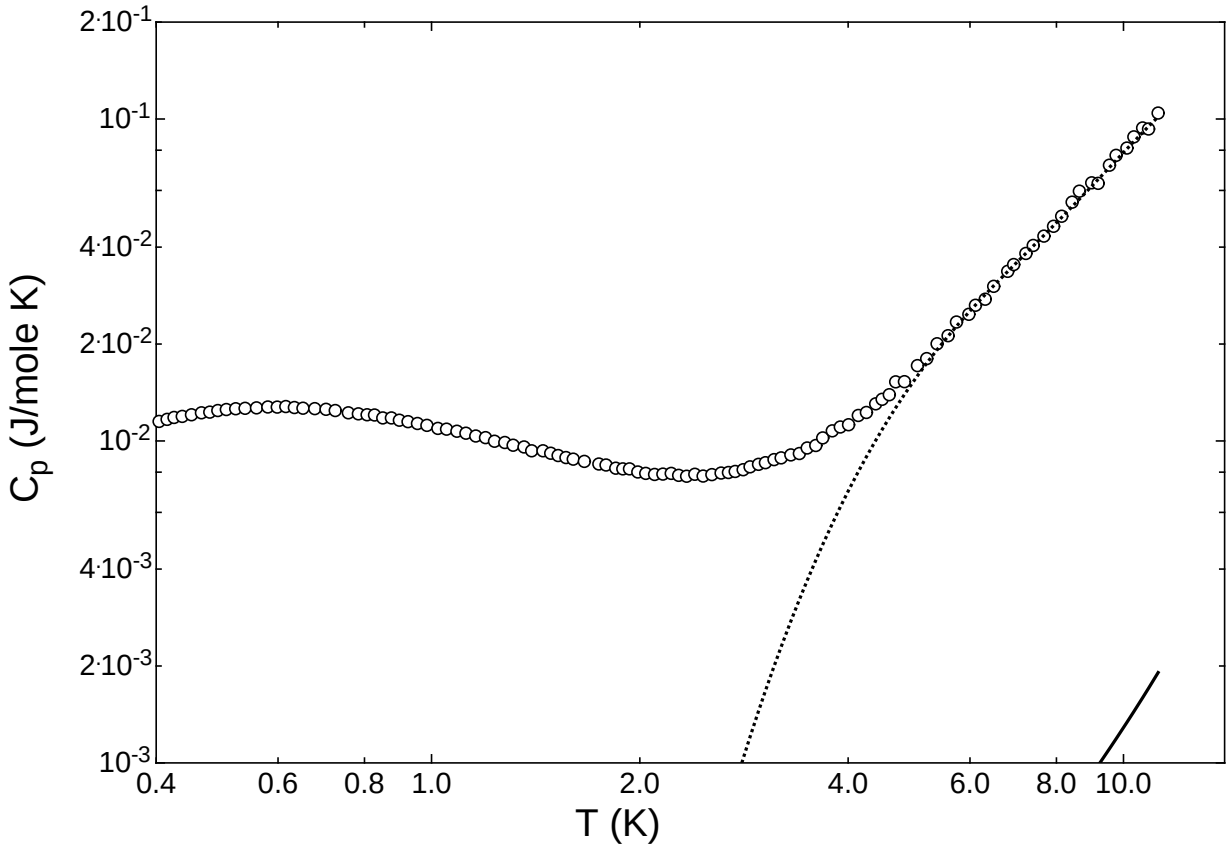

FIG. 2: $C_p(T)$ in zero applied field for $Ca_{0.992}U_{0.008}B_6$ between 0.4 and 12 K. The solid line represents the calculated phonon specific heat, the dotted line is the magnetic specific heat from the next higher magnetic levels.

at $T = 0.61$ K, indicates the formation of a ground state with a strongly enhanced electronic specific heat. The background of the lattice specific heat was calculated by invoking the same model parameters that were used in our calculation of $\rho(T)$ described above. The result is represented by the solid line in Fig. 2. For $T > 6$ K, we attribute the excess specific heat to excitations to higher lying crystal field levels of the 5f electrons. The corresponding fit, indicated by the dotted line in Fig. 2, suggests that the next higher levels are separated from the doublet ground state by $\Delta/k_B = 25$ K. It may be seen that at low temperatures, $C_p(T)$ is dominated by the electronic contribution. Subtracting the mentioned two background contributions from the experimental $C_p(T)$ data results in $C_K(T)$

$$C_K(T) = C_p(T) - C_{lattice}(T) - C_{CEF}(T) \quad , \tag{3}$$

which is plotted as open circles in Fig. 3. This contribution is interpreted as being due

to the Kondo-induced enhanced density of states at the Fermi energy $D(E_F)$. Also shown in Fig. 3 are $C_K(T)$ data in different external magnetic fields.

The maximum of the bell-shaped curve of $C_K(T)$ is, as expected, shifted in magnitude and temperature upon application of external magnetic fields. Our analysis of these data is based on the resonance level (RL) model of Schotte and Schotte [13], which assumes a Lorentzian shape of the electronic density of states $D(\epsilon)$ centered at the Fermi level and given by

$$D(\epsilon) = \Delta/\pi(\epsilon^2 + \Delta^2) \quad . \tag{4}$$

We obtain consistent fits to the experimental curves of $C_K(T, H)$ by postulating $S = 1/2$, setting $\Delta/k_B = 1.6$ K and inserting a g-factor of 1.7. They are shown as solid lines in Fig. 3. The reduction of the g-factor is equivalent to a reduced effective magnetic moment μ_{eff} of the U ions, reflecting the magnetic screening of the local moments by the conduction electrons [13, 14]. Inserting the value for Δ into eq. 4 yields, for $\epsilon = 0$, the density of states $D(E_F)$. Considering that the electronic specific heat parameter γ is given by

$$\gamma = \frac{2}{3}\pi^2 k_B^2 D(E_F) \quad , \tag{5}$$

we obtain $\gamma = 92$ mJ/(K^2·mole-U). For comparison, we calculate γ' for the case of an ordinary conduction band with a quadratic dispersion relation and populated by one electron per U-ion. The effective mass is $m^* = 0.28 \cdot m_0$, the same as for itinerant charge carriers in CaB_6 [15]. With these assumptions, we obtain $\gamma' = 0.19$ mJ/(K^2·mole-U), implying that the Kondo interaction leads to an enhancement of the specific heat parameter by

$$\gamma_K/\gamma' \approx 480 \quad . \tag{6}$$

For $T \gg T_K$, the conduction electrons are incoherently scattered by the actinide ions and the corresponding magnetic moments may be regarded as isolated and only weakly coupled via the RKKY interaction. Consequently, above 50 K, the susceptibility $\chi(T)$, measured in an external magnetic field of 0.1 T and at temperatures between 2 and 330 K, can be fitted by a Curie-Weiss type law, with $J = 9/2$, $g_J = 8/11$ and a paramagnetic Curie temperature of $\Theta_p \approx$ - 5.9 K. The T^{-1} dependence is riding above a constant paramagnetic background of $\chi_0 = 3.15 \cdot 10^{-5}$. In our context, we concentrate on the low-temperature features of $\chi(T)$

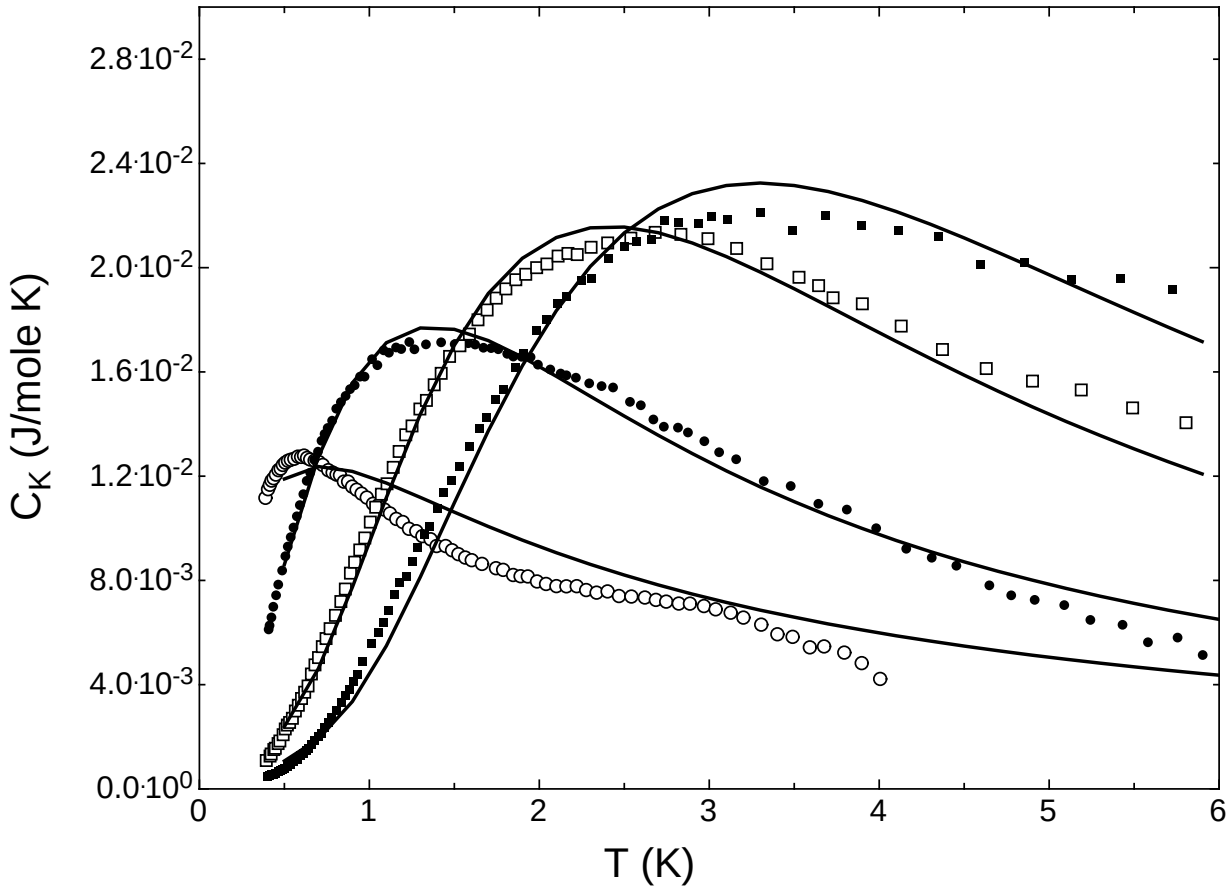

FIG. 3: Kondo-induced electronic part of the specific heat $C_K(T,H)$ for $Ca_{0.992}U_{0.008}B_6$ between 0.4 and 6 K and at magnetic fields of $H = 0$ kOe (empty circles), 25 kOe (filled circles), 50 kOe (empty squares) and 70 kOe (filled squares). The solid lines show the calculations according the resonance-level model [13] described in the text.

and $M(H)$. The available data sets below 8 K are displayed in Fig. 4. In order to be consistent with the specific-heat analysis, the susceptibility $\chi(T)$, taken as $M(H,T)/H$ at low magnetic fields H, was interpreted by again employing the RL model of Schotte and Schotte [13]. Their general expression of $\chi(T)$ reduces, for $S = 1/2$, to the equation first presented by Rivier and Zuckermann [16], who considered localized spin fluctuations in a dilute non-magnetic alloy. The results of the calculation, using the same parameters for the resonance width Δ, the g-factor and the spin S as quoted above, is displayed as solid lines in Fig. 4 for both $\chi(T)$ in the main frame, and $M(H,T)$ in the inset, respectively. It is particularly rewarding that both magnetic and specific-heat data can be well reproduced even quantitatively with this simple model. Of course, all these considerations are only valid

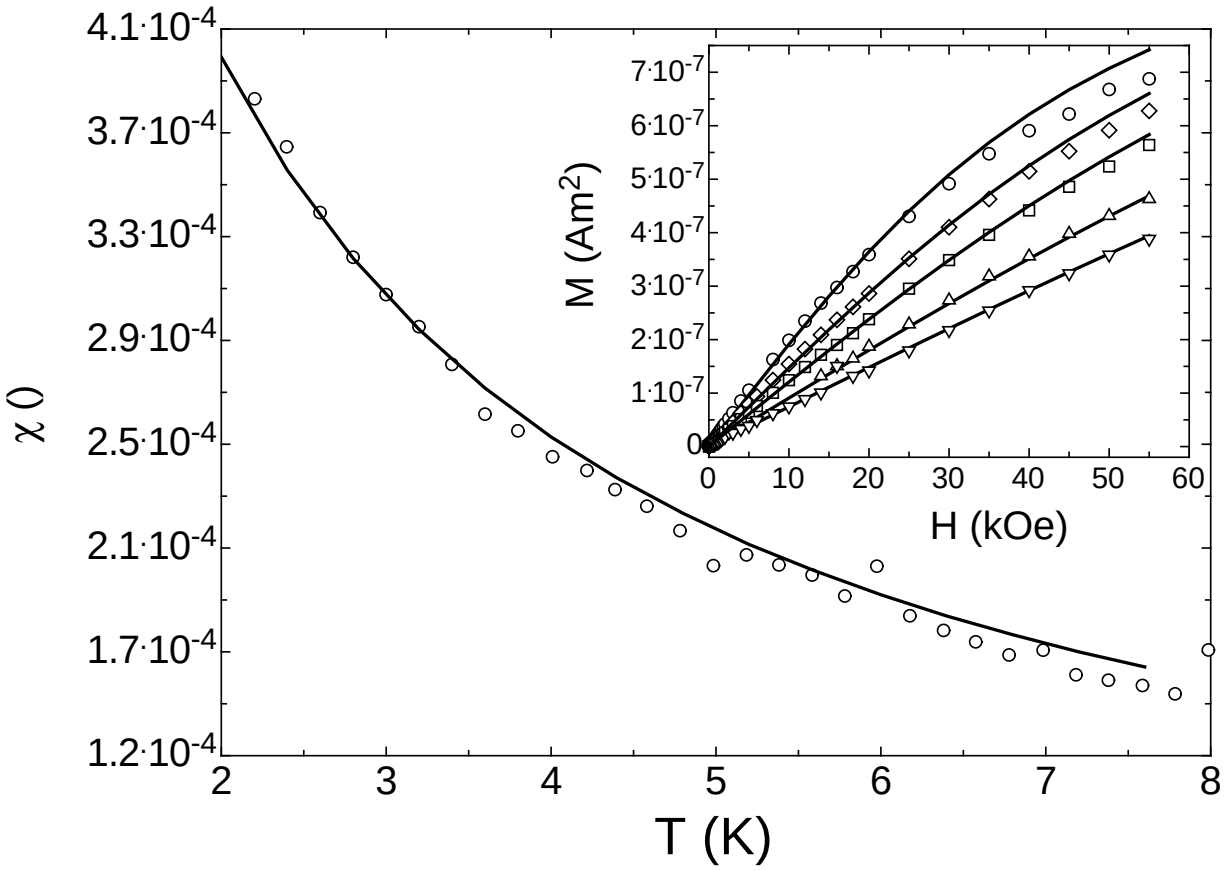

FIG. 4: $\chi(T)$ at $H_{app} = 1$ kOe for $Ca_{0.992}U_{0.008}B_6$. The inset shows $M(H)$ for $T = 2$ K (circles), 3 K (diamonds), 4 K (squares), 6 K (triangles up) and 8 K (triangles down). The solid lines describe the calculations according to the model of Schotte and Schotte described in the text.

at low temperatures, where the Kondo induced features dominate the electronic properties.

Most earlier experimental attempts to demonstrate the onset of the Kondo effect due to U impurities were either unsuccessful or did not provide conclusive results. Previous work on the influence of U replacing La in $LaAl_2$, e.g., claimed the first observation of the Kondo effect in a dilute actinide alloy [17]. We believe that, in retrospect, the experimental evidence for that claim is not convincing. We argue that also in that case, the local moment character of the U ions was not well enough developed. Some indications for a Kondo-type behaviour of the resistivity [18] and the low-temperature specific heat [19] data were reported for compounds of the type $Th_{1-x}U_xSe$ and $Th_{1-x}U_xS$ in the range $0.06 < x < 0.26$. The available data did not allow to unambiguously distinguish between Kondo-behaviour [19] and a mixed-valence situation [18]. A logarithmic T-dependence with a negative slope of

$\rho(T)$ was also reported for $Th_{0.86}U_{0.14}Sb$ [20]. Again, the situation seems ambiguous and a mixture of mixed-valency and Kondo effect cannot be excluded [21]. Our data, however, indicate that the insertion of U at the low at. % level into a matrix with a very low conduction electron concentration, such as CaB_6, favors the stability of the local moment on the U site, leading to a well developed classical Kondo effect at low temperatures.

In conclusion, we have demonstrated, by means of resistivity, specific heat and magnetization measurements, that a Kondo-type behaviour by dilute impurities of U can be achieved by placing U onto cation sites of the low-density itinerant carrier matrix CaB_6. Replacing La by U in concentrations of the order of 1 % in LaB_6 does not lead to Kondo features at temperatures above 0.4 K. In order to establish the reason for the formation of localized 5f electrons on the U sites in CaB_6 but not in LaB_6, additional information from, e.g., optical experiments and theoretical considerations is required.

We appreciate stimulating discussions with R. Monnier. This work has benefited from partial financial support of the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung and the US-NSF grant DMR-0433560.

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